

Dissolution of copper precipitates in Czochralski silicon

S.A. McHugo^{1,2}, A.C. Thompson¹, A. Mohammed¹ and C. Flink^{2,3}

¹Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

²Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

³University of Köln, Physics Department, Köln, Germany

INTRODUCTION

Transition metal contamination of silicon is of significant concern in the semiconductor industry. These impurities are fast diffusers with high solubilities at moderate to high temperatures [1], which can be easily introduced from stainless steel and copper tools during ingot growth and processing. The metal impurities can exist in a dissolved or precipitated state within the silicon, both of which produce deleterious effects. Dissolved transition metals can form deep levels, which enhance carrier recombination and generation while precipitated impurities form energy bands, which enhance recombination, generation and can create electrical shorts. Carrier generation increases the background noise of a charge-coupled device (CCD) [2] and increases the base current in bipolar devices [3]. Furthermore, since it has been demonstrated that metal impurities segregate to or precipitate at the Si/SiO₂ interface [4], or they become trapped in the oxide [5]. The presence of metal impurities can degrade the dielectric strength of thin oxide layers, leading to gate oxide integrity (GOI) failures [6].

Removal of impurities from active device regions is generally referred to as gettering. For integrated circuit (I.C.) devices, gettering is performed with structural defects in the bulk of the material, which act as precipitation sites for metal impurities such that, with proper heat treatments, the near-surface, active device region becomes devoid of metal impurities. These structural defects are oxygen precipitates and growth-related defects such as stacking faults and dislocation loops. Since the oxygen is present after growth of the silicon crystal, this type of gettering is generally referred to as intrinsic or internal gettering [7, 8].

Effective gettering is becoming increasingly important in the I.C. industry. The demand for increased chip performance is driving the use of new materials such as Cu interconnects [9, 10], silicon-on-insulator, polysilicon backside layers [11], new high K [12] and low K dielectric films [13], all of which can introduce unwanted impurities into the active device region. Since Cu diffuses rapidly through silicon in high concentration, the use of Cu interconnects brings an added risk of device failure. While in-diffusion barriers such as TaN are implemented to prevent Cu introduction into the silicon, their effectiveness has not been quantified. Typically, internal gettering sites are used to remove any Cu atoms unintentionally introduced into the silicon, essentially acting as a safety net during Cu interconnect implementation.

Past studies of Cu in silicon have focussed on the dissolved state of Cu, Cu diffusivity and solubility. This includes the behavior of Cu-Cu pairs, Cu-dopant pairs and interstitial Cu. Little work has been performed on the formation and dissolution of Cu precipitates, which is critical to understand the interaction of Cu with the internal gettering sites and the effectiveness of this safety net.

The studies presented here are on copper precipitates in silicon with a focus on the ability to retain or remove metal impurities away from the active device region of integrated circuits with the use of internal gettering sites. With x-ray fluorescence microscopy, we have studied the dissolution rate of copper precipitated at internal gettering sites as a function of temperature. We observe Cu precipitate dissolution even with low temperature anneals, which are commonly used in the final stages of I.C. processing. This dissolution indicates Cu contamination of the device region may occur from Cu previously gettered to internal gettering sites.

RESULTS

Cu was in-diffused into Czochralski silicon with 10^{11} oxygen precipitates/cm³ at 1170°C for 2 hours. With this time and temperature, a Cu concentration of 10^{17} atoms/cm³ is introduced uniformly throughout the sample. The samples were rapidly removed from the annealing furnace and allowed to cool in air with an initial cooling rate of $\approx 25^\circ\text{C}/\text{sec}$. Considering the high mobility of Cu even near room temperature, we expected the majority of Cu to precipitate at the oxygen precipitates and their growth-related defects. We measured the spatial distribution of Cu with the x-ray fluorescence (XRF) microprobe at beamline 10.3.1. The microprobe can detect one 20nm radii Cu precipitate in a $\approx 50\mu\text{m}^3$ volume over hundreds of microns. No standard technique provides such high sensitivity with large sampling volume, making the microprobe invaluable for these studies.

XRF scans of the samples following in-diffusion and air cooling are shown in Figures 1a and b. The dashed box indicates the region of overlap with later scans. Note the volumetric density is many orders of magnitude lower than the oxygen precipitate density. However, the density of stacking faults, formed during oxygen precipitate formation, is typically many orders of magnitude lower than the oxygen precipitate density, indicating the preferred precipitation site for the Cu are stacking faults. Further work will be preformed to confirm this implication.

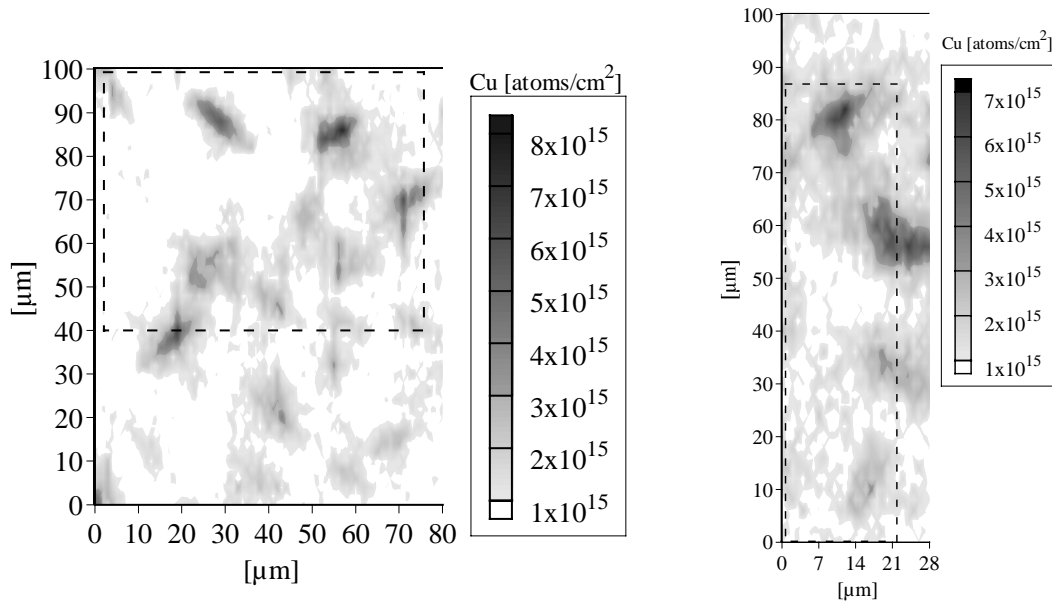


Figure 1a

Figure 1b

The samples were annealed either at 360°C or 460°C for 30 minutes for the regions in 1a and 1b, respectively to dissolve the Cu precipitates. XRF scans were taken in the same regions following the dissolution anneals. The scans are shown in Figures 2a and b for the 360°C and 460°C anneals, respectively. The dashed box indicates the region of overlap with the scans in Figures 1a and 1b. Note the disappearance of some of the Cu precipitates as well as a decrease in the Cu signal at other precipitate sites, signifying the Cu precipitates are dissolving back into the silicon matrix. This dissolution at temperatures as low as 360°C, indicates that even the low temperature processing steps found in the final steps of I.C. processing may release Cu back into the silicon matrix and into the active device region of the I.C. device.

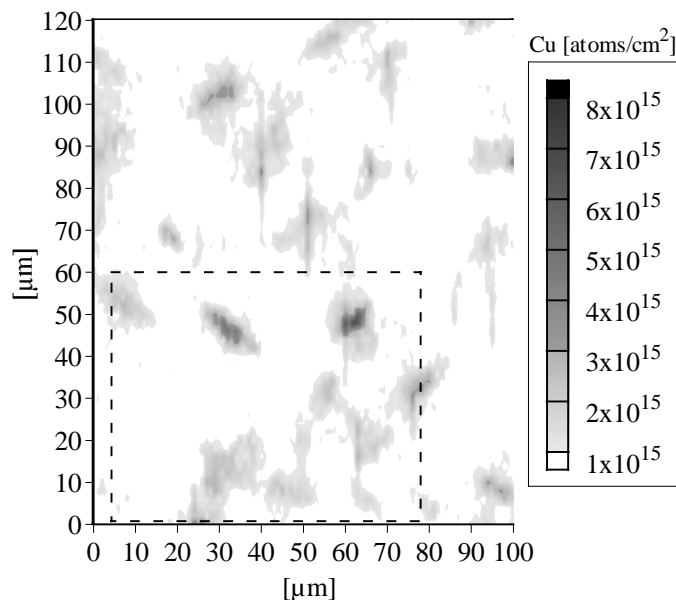


Figure 2a

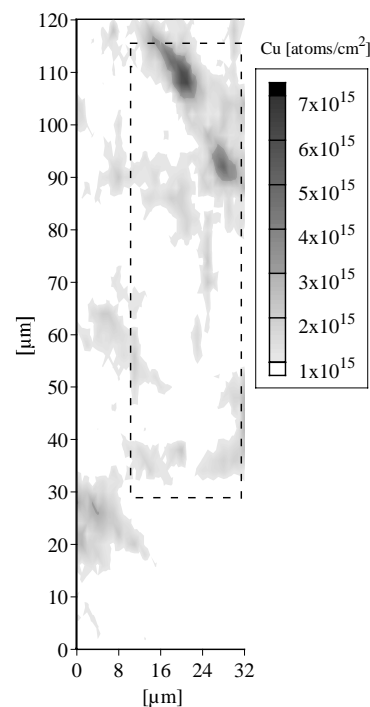


Figure 2b

ACKNOWLEDGMENTS

The authors would like to thank R. Gunion, R. Tackaberry, A. MacDowell and R. Celestre for their help with the experiments as well as E.R. Weber, Z. Hussain and H. Padmore for their edifying discussions. We would also like to thank R. Falster for providing well-defined samples.

REFERENCES

1. E. R. Weber, *Appl. Phys. A*, **30**, 1, (1983)
2. W. C. McColgin, J. P. Lavine and C. V. Stancampiano, Proceedings of the Materials Research Society, Symposium: Defects in Electronic Materials II, San Francisco, 187-92, (1997)
3. R. F. Pierret, "Semiconductor Device Fundamentals." 1996 Addison-Wesley. Reading, MA.
4. T. Kitano, *J. Elec. Matls.* **21**, 1027-1031, (1992)
5. K. Honda, A. Ohsawa and T. Nakanishi, *J. Electrochem. Soc.* **142**, 3486, (1995)
6. E. P. Burte and W. Aderhold, *Solid-State Electron. (UK)*. **41**, 1021-5, (1997)
7. W. K. Tice and T. Y. Tan, *Mat. Res. Soc. Symp. Proc.* **2**, 367-380, (1981)
8. D. Gilles, E. R. Weber and S. K. Hahn, *Phys. Rev. Lett.* **64**, 196, (1990)
9. J. N. Burghartz, D. C. Edelstein, K. A. Jenkiin and Y. H. Kwark, *IEEE Transactions on Microwave Theory and Techniques*. **45**, 1961-8, (1997)
10. L. Geppert, *IEEE Spectrum*. **36**, 52-6, (1999)
11. M. B. Shabani, T. Yoshimi, H. Abe, T. Nakai and B. Cordts, Proceedings of Seventh International Symposium on Silicon-on- Insulator Technology and Devices, Los Angeles, CA, USA, 162-75, (1996)
12. S. R. Gilbert, B. W. Wessels, D. B. Studebaker and T. J. Marks, *Appl. Phys. Lett.* **66**, 3298-300, (1995)
13. S. McClatchie, K. Beekmann and A. Kiermasz, *European Semiconductor*. **21**, 32-3, (1999)

Funding for this work is by the National Renewable Energy Laboratory (NREL) under contract number XAF-8-17607-04 and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

Principal investigator: Scott McHugo, Advanced Light Source, Ernest Orlando Lawrence Berkeley National Laboratory. Email: samchugo@lbl.gov. Telephone: 510-486-4874.